(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 447 138 A1

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: 91301960.0

(51) Int. Cl.[5]: G03C 7/30

(22) Date of filing: 08.03.91

(30) Priority: 14.03.90 JP 63615/90

(43) Date of publication of application:
18.09.91 Bulletin 91/38

(84) Designated Contracting States:
DE GB IT NL

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(54) **Color photographic light-sensitive material.**

(57) A silver halide color photographic light-sensitive material is disclosed. The material comprises a support, and, coated thereon, a blue-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer and a red-sensitive silver halide emulsion layer, each layer containing a sensitizing dye, wherein the maximum sensitivity wavelength λ Rmax, maximum sensitivity SRmax and sensitivity at 610 nm SR_{610} of the red-sensitive emulsion layer and the maximum sensitivity wavelength λ Gmax, maximum sensitivity SGmax, and sensitivity at 545 nm SG_{545} of the green-sensitive emulsion layer satisfy the following requirements:

$$590 \text{ nm} \leq \lambda \text{ Rmax} \leq 625 \text{ nm}, \quad SR_{610} \geq 0.8 \text{SRmax}$$
$$520 \text{ nm} \leq \lambda \text{ Gmax} \leq 570 \text{ nm}, \quad SG_{545} \leq 0.8 \text{SGmax}$$

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Interimag effect using a so-called diffusible DIR or another appropriate means as commonly known.

It was found, however, that even any combination of the methods described above offers nothing more than extremely unsatisfactory color reproduction in the case of picture taking under fluorescent lamp or under mixed light of strobe light and fluorescent lamp. Specifically, when using a fluorescent lamp light source alone or even when using strobe light under the influence of a fluorescent lamp, the reproduced colors tend to be greenish, particularly the reproduced skin color lacks liveliness.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a color photographic light-sensitive material with high sensitivity which offers exact color reproduction not only under daylight picture taking conditions but also under fluorescent lamp picture taking conditions.

DETAILED DESCRIPTION OF THE INVENTION

The present inventors made intensive investigations and found that the object of the invention described above can be accomplished by a silver halide color photographic light-sensitive material having at least one blue-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer and at least one red-sensitive silver halide emulsion layer on the support, wherein the maximum sensitivity wavelength λR_{max}, maximum sensitivity SR_{max} and sensitivity at 610 nm SR_{610} of the red-sensitive emulsion layer and the maximum sensitivity wavelength λG_{max}, maximum sensitivity SG_{max} and sensitivity at 545 nm SG_{545} of the green-sensitive emulsion layer satisfy the following requirements:

$$590nm \leqq \lambda R_{max} \leqq 625nm \quad SR_{610} \geqq 0.8\ SR_{max}$$

$$520nm \leqq \lambda G_{max} \leqq 570nm \quad SG_{545} \leqq 0.8\ SG_{max}$$

The present invention is hereinafter described in more detail.

With respect to color reproduction in picture taking under different kinds of light sources, focus of discussion has been placed on light source color temperature, and a large number of proposals have been made for technical improvements. In recent years, however, there have been frequent occurrence of troubles in picture taking under fluorescent lamp lighting as fluorescent lamps have become commonly used lighting equipment in daily life.

A typical claim is that pictures taken in the presence of fluorescent lamp light are so greenish that the face of a person photographed lacks liveliness. This was found to be due to the spectral distribution of fluorescent lamp light consists of two components, one having a continuous smooth curve in the visible region and the other having a bright line (characteristic curve) in a particular wavelength region, and is sensed as strongly greenish, less reddish by color films while being felt white by human eyes. On a related note, there are numerous kinds of fluorescent lamps, and the so-called three-wavelength fluorescent lamp, which has recently gained wide popularity as ordinary household appliance, was found to expand the color shift described above in color photography because of the great contribution of the bright line.

The present inventors found that the problem described above can be well overcome by setting the spectral sensitivity distribution at a minimum density (D_{min}) + 0.3 so that the green- and red-sensitive layers fall in the relationship described in the claim of the invention.

In a preferred mode of the present invention, it is more preferable that the sensitivity at 610 nm, SR_{610} exceed 90% of the maximum spectral sensitivity, SR_{max} in the spectral sensitivity distribution $SR(\lambda)$ of the red-sensitive layer at a density of D_{min} + 0.3.

Also, to efficiently obtain the desired spectral sensitivity, it is preferable to adsorb the sensitizing dyes of the present invention contained in the green- and red-sensitive layers upon the chemical sensitization of the silver halide.

To obtain the spectral sensitivity distribution in the red-sensitive layer of the present invention, various means can be used, including the use of a spectral sensitizing dye. This constituent can be obtained by a combination of at least one sensitizing dye represented by the formula I and at least one sensitizing dye represented by the formula III, and the sensitizing dye represented by the formula I is used in an amount of 10 to 90 mol%, preferably 60 to 90 mol%, based on the total amount of dyes used. It is also possible to combine at least one of the formula I, at least one of the formula II and at least on of the formula III.

The sensitizing dyes represented by formulas I, II and III are described below.

wherein R_{11} represents a hydrogen atom, an alkyl group or an aryl group; R_{12} and R_{13} independently represent an alkyl group or an aryl group. Also, Y_3 and Y_4 independently represent a sulfur atom or a selenium atom.

Z_9, Z_{10}, Z_{11} and Z_{12} independently represent a hydrogen atom, a halogen atom, a hydroxyl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an acyloxy group, an aryloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkoxycarbonylamino group, a sulfonyl group, a carbamoyl group, an aryl group, an alkyl group or a cyano group. Z_9 and Z_{10} and/or Z_{11} and Z_{12} respectively may link together to form a ring. $X_3^{\ominus}$ represents an anion. n represents the integer 1 or 2; when the sensitizing dye forms an intramolecular salt, n represents 1.

Typical examples of the sensitizing dyes represented by formulas I, II and III are given below.

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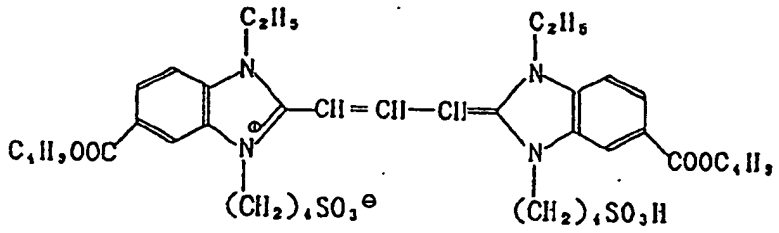

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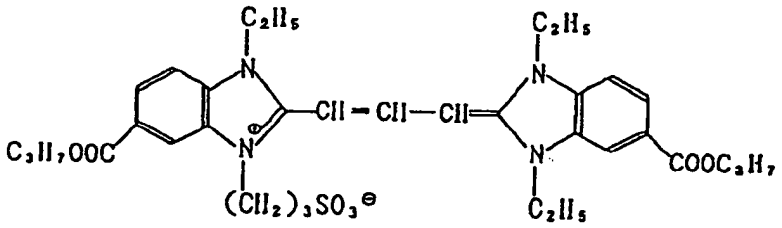

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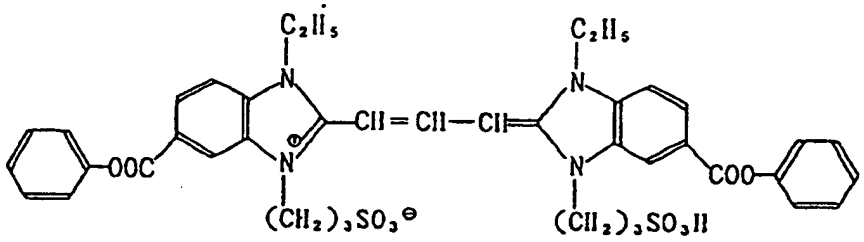

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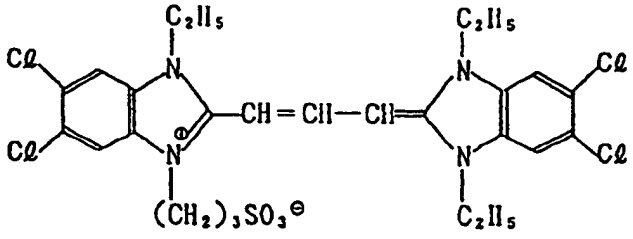

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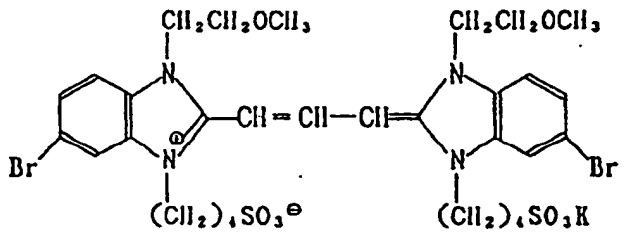

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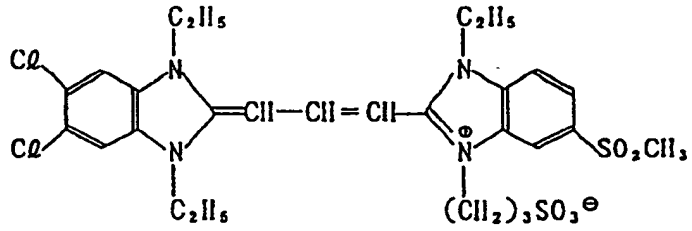

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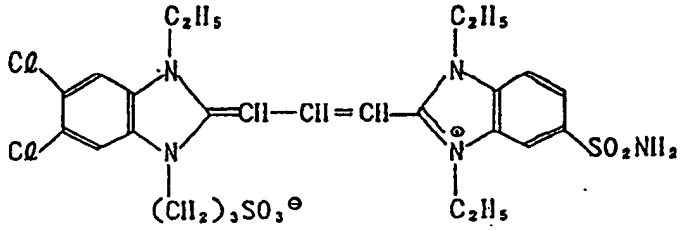

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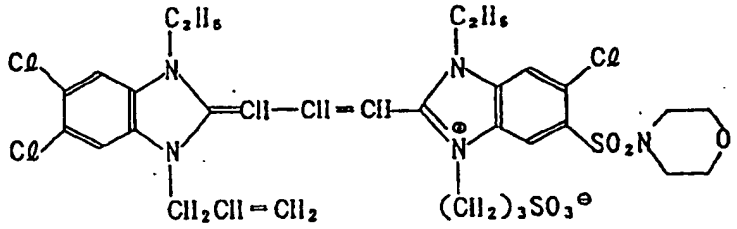

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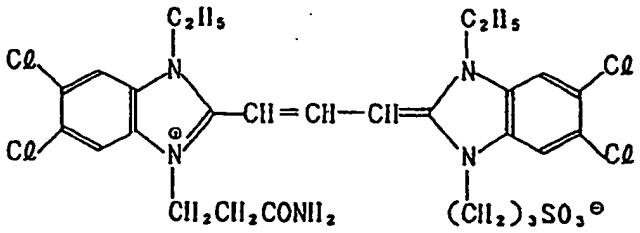

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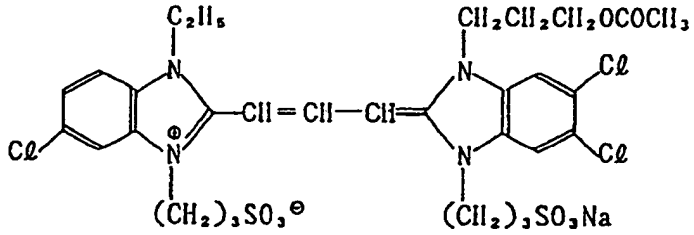

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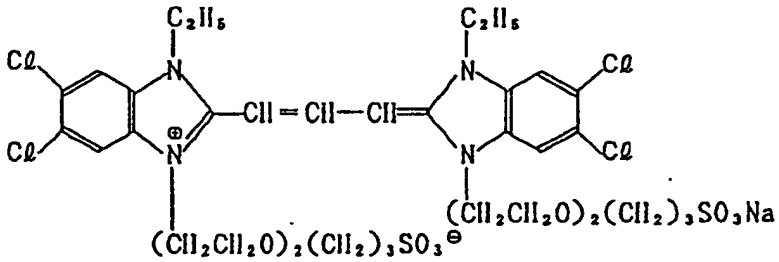

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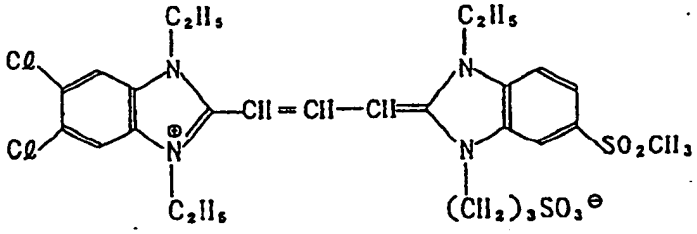

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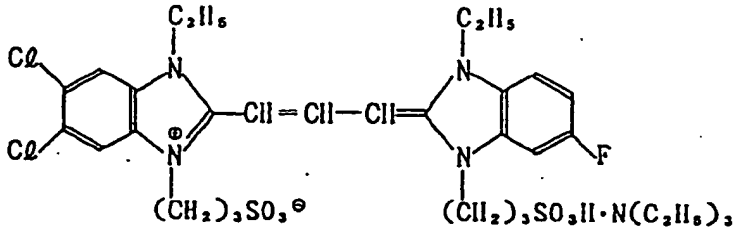

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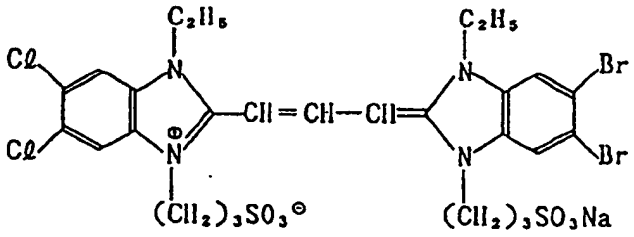

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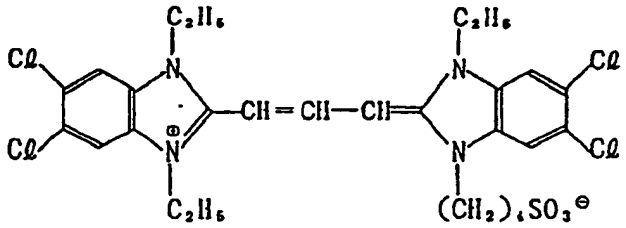

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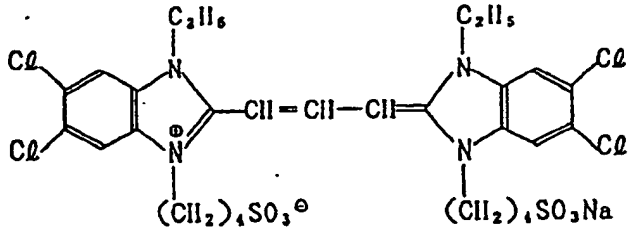

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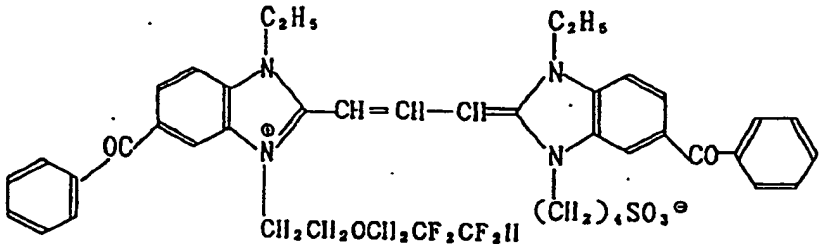

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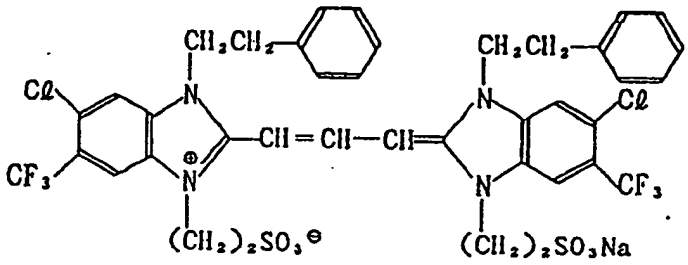

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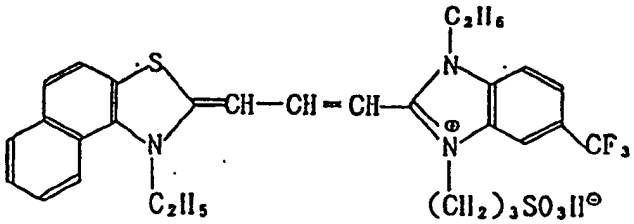

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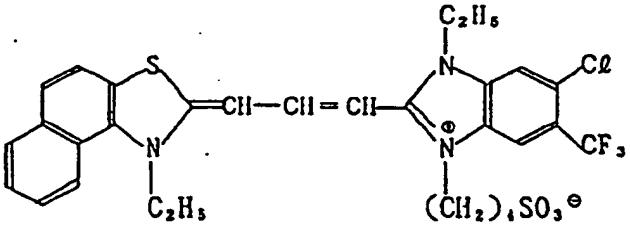

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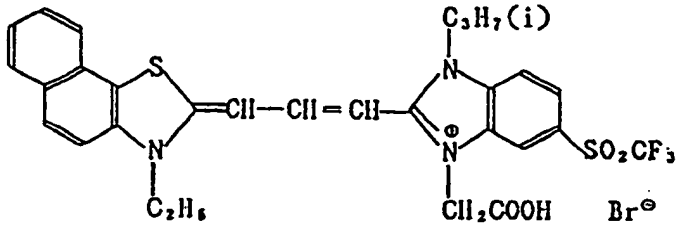

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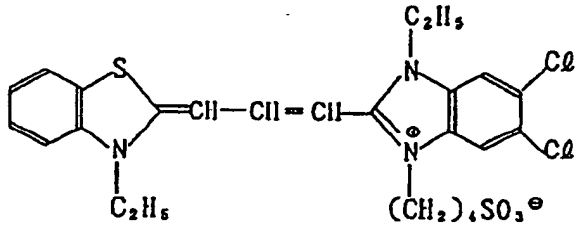

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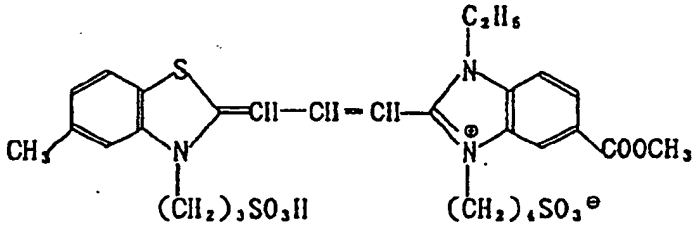

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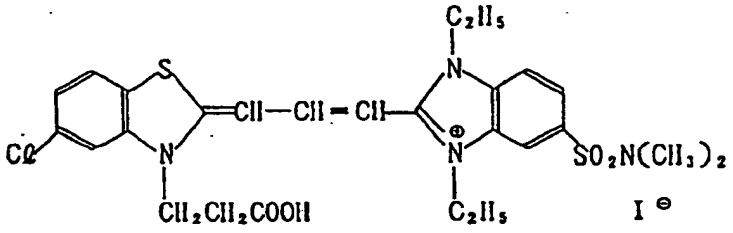

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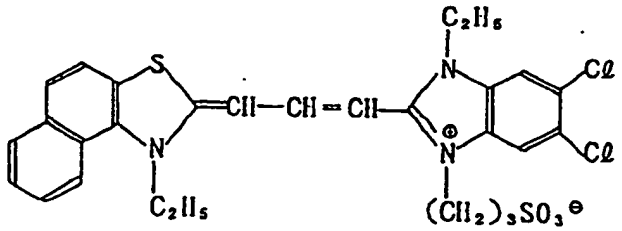

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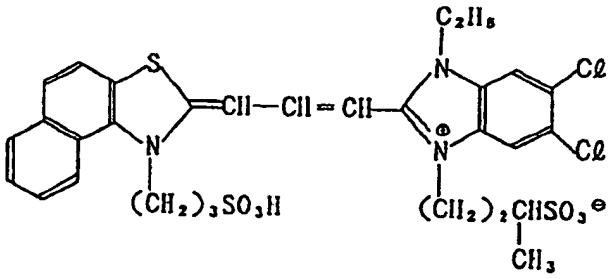

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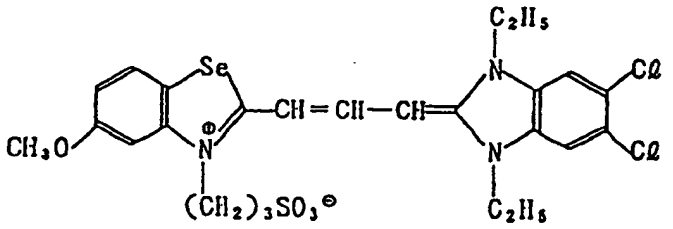

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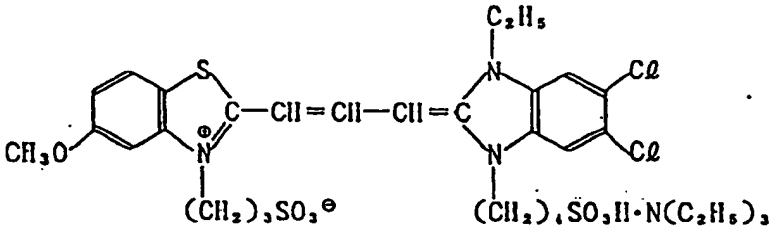

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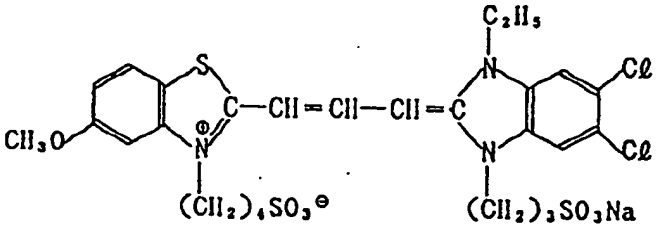

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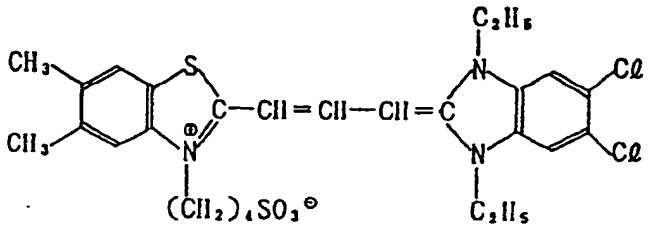

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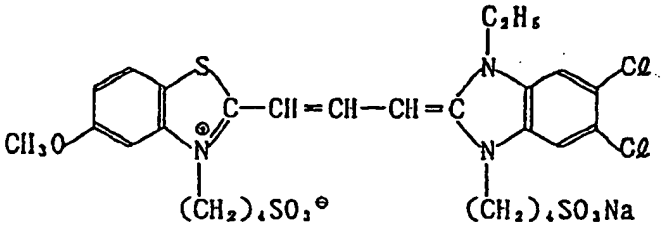

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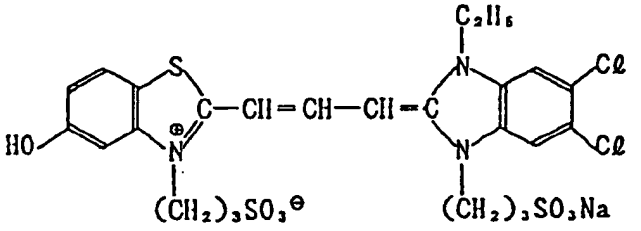

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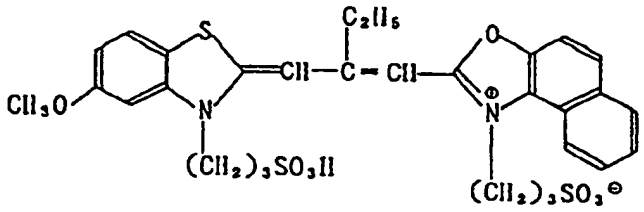

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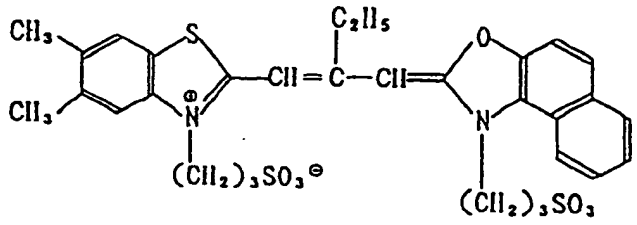

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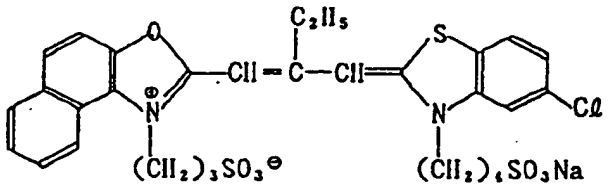

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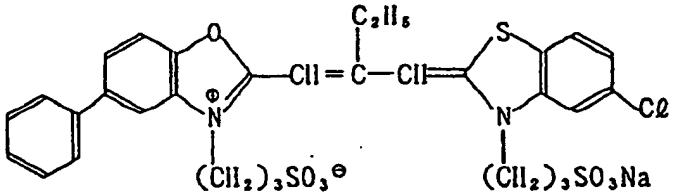

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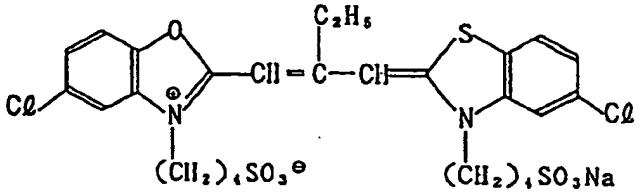

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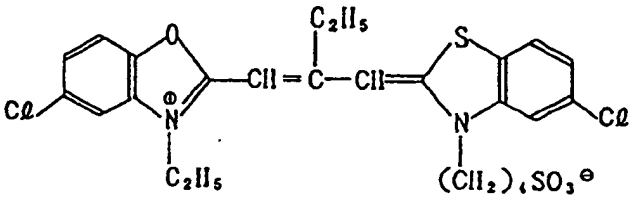

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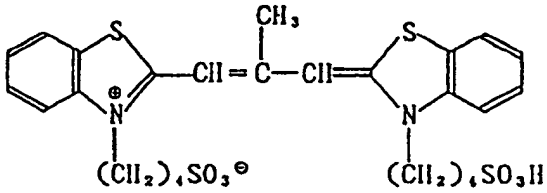

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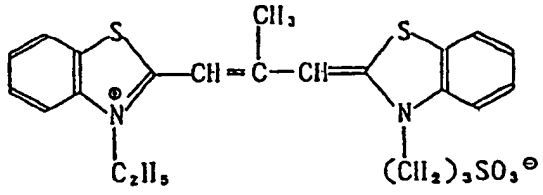

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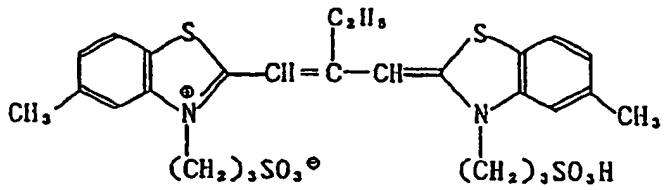

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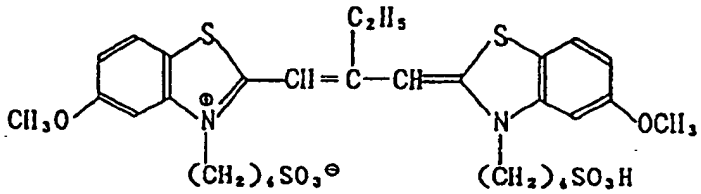

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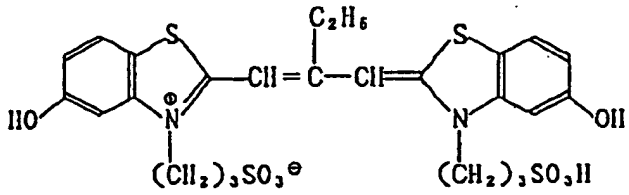

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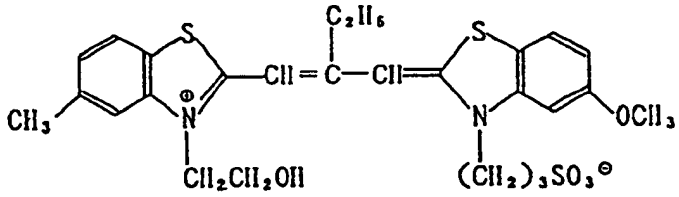

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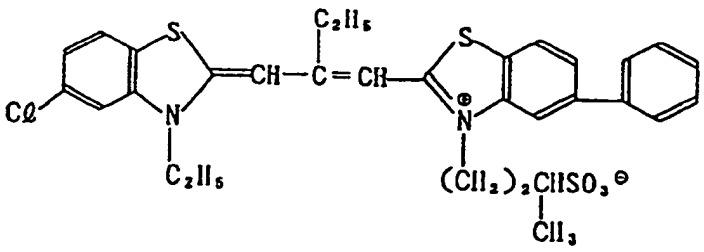

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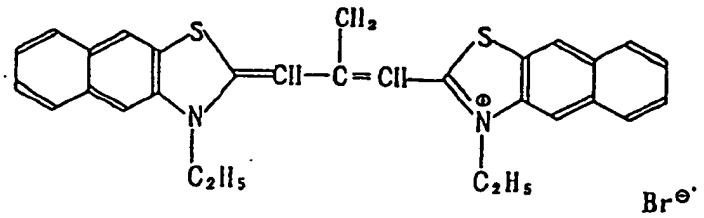

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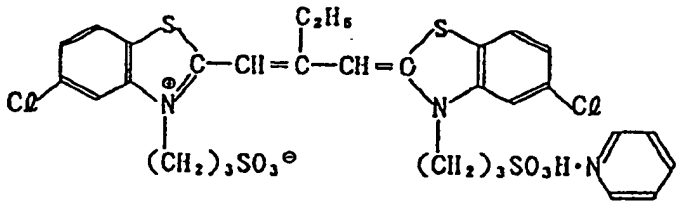
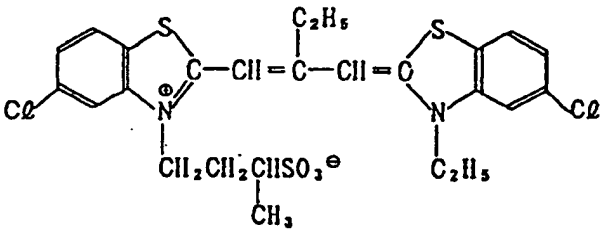
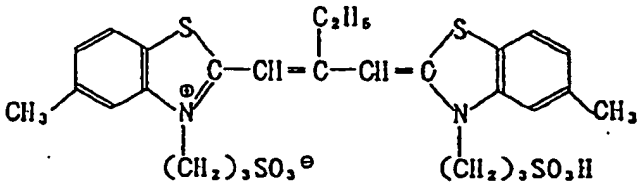


(III—18)



(Ⅲ—23)



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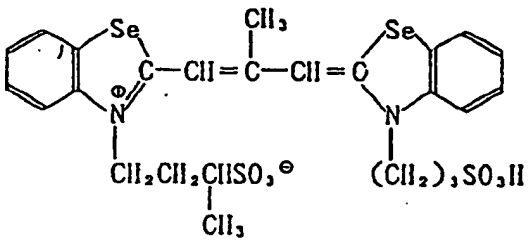

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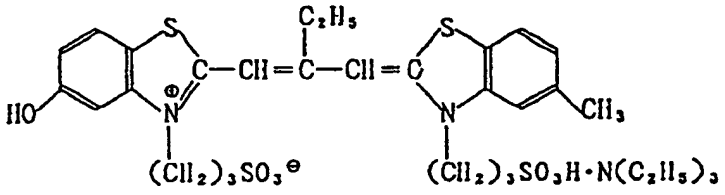

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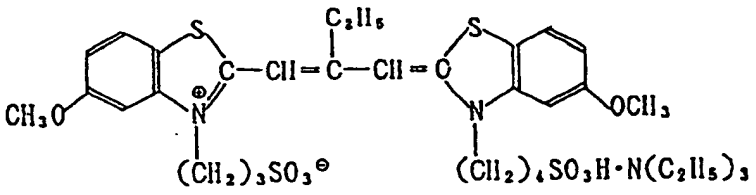

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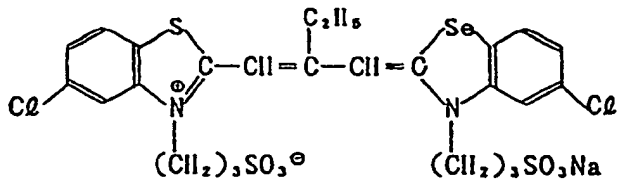

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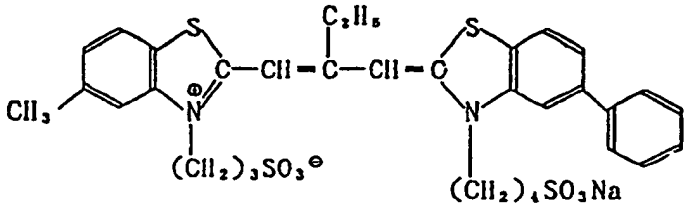
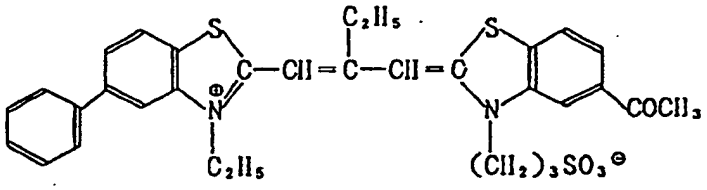


(Ⅲ—33)



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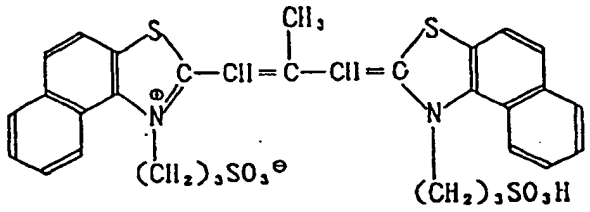

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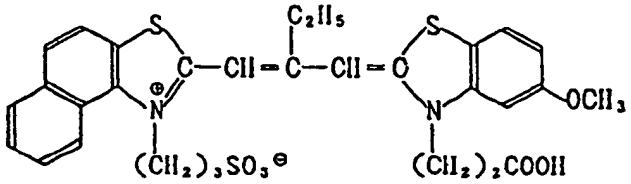
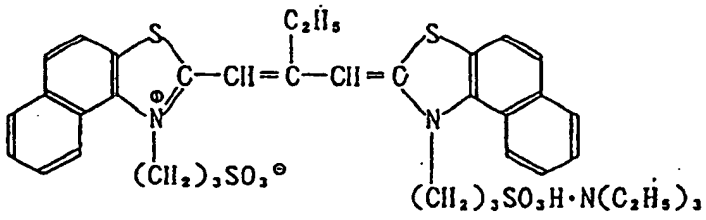
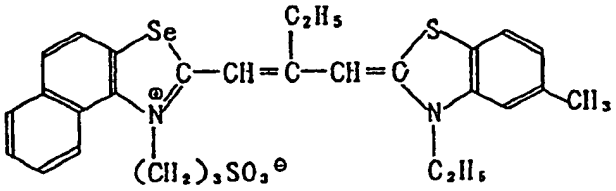


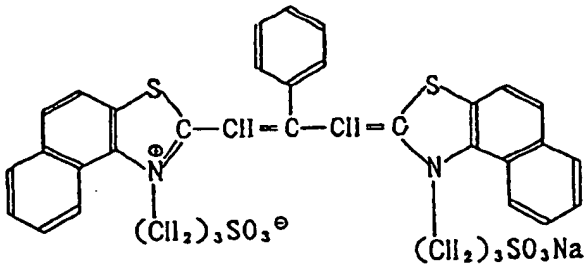
(Ⅲ—40)



(Ⅲ—41)



(Ⅲ—42)

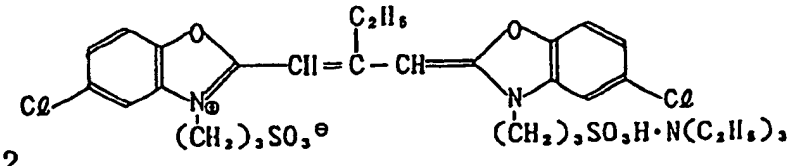


Typical examples of the sensitizing dye oxacabocyanine, oxabenzimidazolecyanine, thia-4' -cyanine or thia-2' -cyanine dyes, which can be used for th green-sensitive layer of the present inv ntion is given below, but these are not to be construed as limitative n th invention.

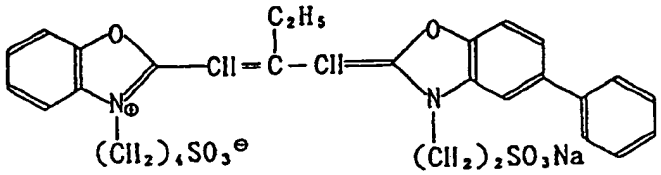
The green-sensitiv emulsion layer of the invention contains oxacabocyanine, oxabenzimidazolecyanine, thia-4' -cyanine or thia-2' -cyanine dyes in an amount of 50 to 80 mol% based on the total amount of a sed-sitezing dye in it.

It is also possible to use the preceding sensitizing dyes represented by formula I or II which can be used to control the spectral sensitization distribution in the red-sensitive layer.

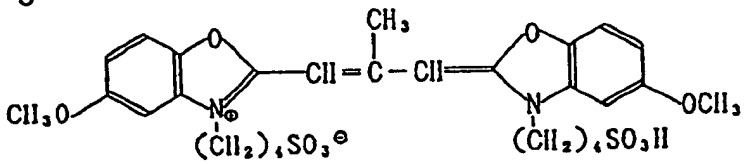
IV − 1



IV − 2



IV − 3



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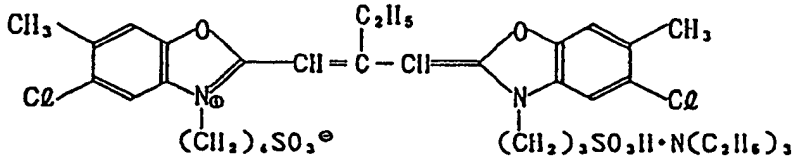

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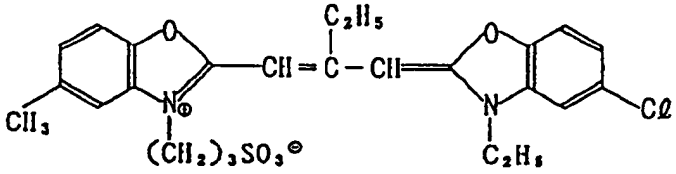
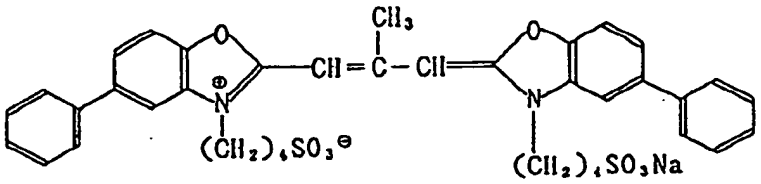


IV－11



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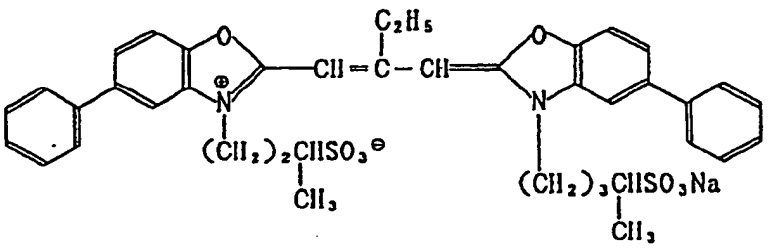

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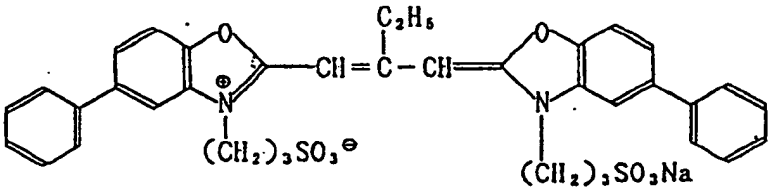

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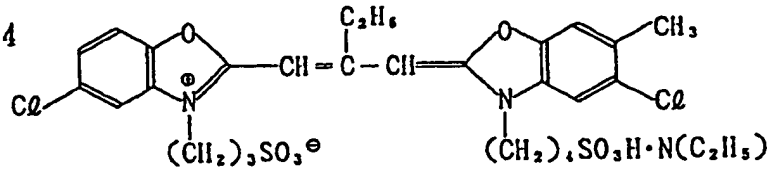

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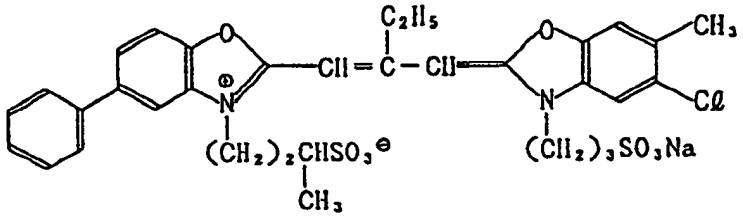

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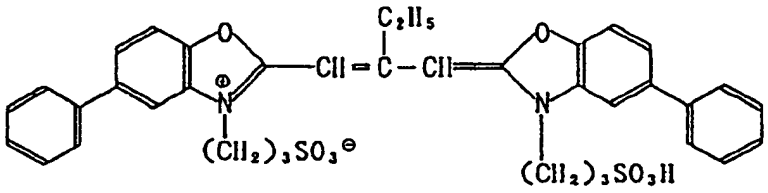

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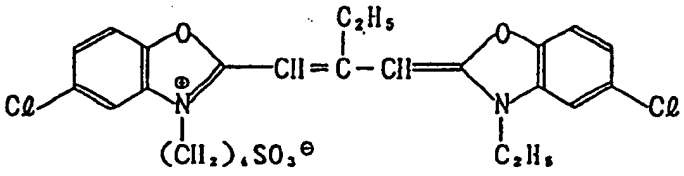
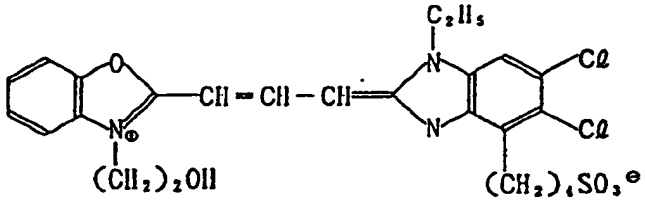
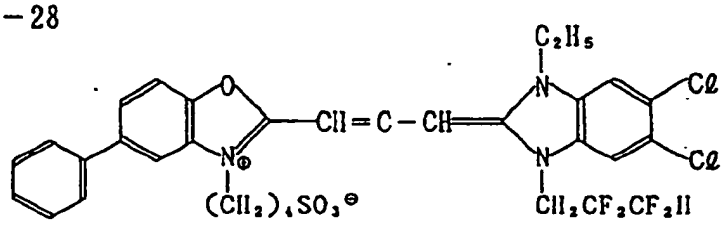


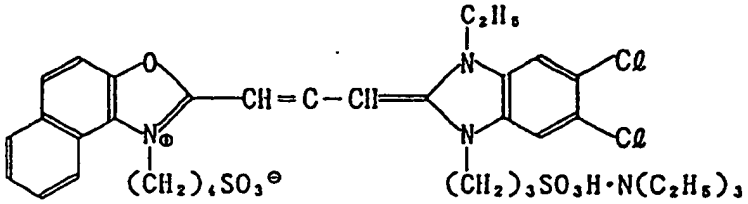
IV－22



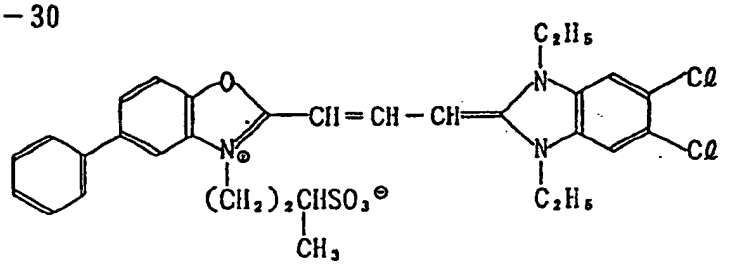
IV－28



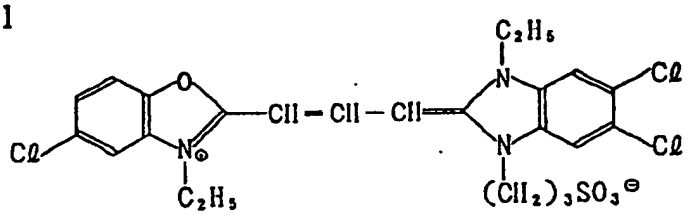
IV－29



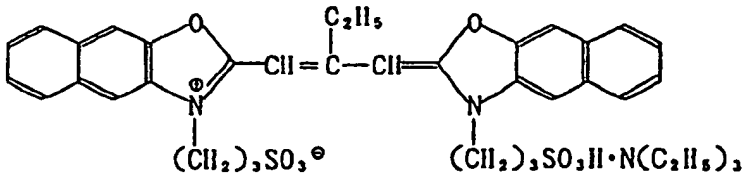
IV－30



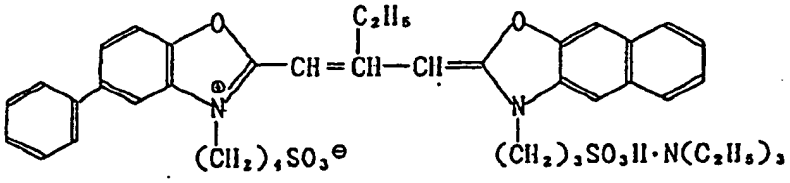
IV－31



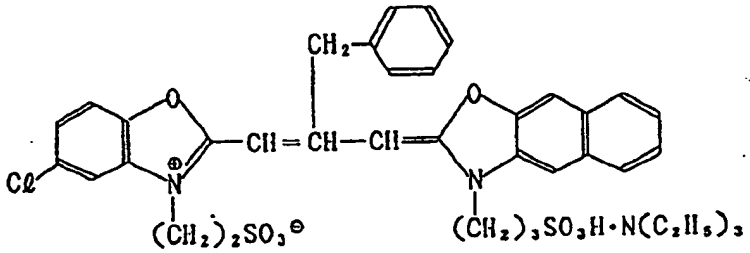
IV – 39



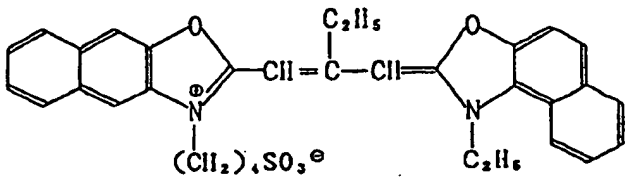
IV – 40



IV – 41



IV – 42



[Item]	[page in RD308119]	[RD17643]	[RD18716]
Antistaining agent	1002 VII-I	25	650
Dye image stabilizer	1001 VII-J	25	
Whitening agent	998 V	24	
UV absorbent	1003 VIII-C, XIII C	25-26	
Optical absorbent	1003 VIII	25-26	
Light scattering agent	1003 VIII		
Filter dye	1003 VIII	25-26	
Binder	1003 IX	26	651
Antistatic agent	1006 XIII	27	650
Hardener	1004 X	26	651
Plasticizer	1006 XII	27	650
Lubricant	1006 XII	27	650
Activator, coating aid	1005 XI	26-27	650
Matting agent	1007 XVI		
Developer (contained in the sensitive material)	1011 XX B		

Various couplers can be used for the present invention. Examples thereof are described in the above Research Disclosures.

The table below specifies where relevant description appears.

Layer 2: First interlayer IL-1

Gelatin	1.3
UV absorbent UV-1	0.1
High boiling solvent Oil-1	0.1

Layer 3: Low speed red-sensitive emulsion layer RL

Silver iodobromide emulsion Em-1	0.8
Sensitizing dye III-40	2.4×10^{-5}
Sensitizing dye III-6	1.9×10^{-4}
Sensitizing dye II-40	1.9×10^{-4}
Cyan coupler C-1	0.70
Colored cyan coupler CC-1	0.10
DIR compound D-1	0.03
DIR compound D-3	0.01
High boiling solvent Oil-1	0.64
Gelatin	1.2

Layer 4: Moderate speed red-sensitive emulsion layer RM

Silver iodobromide emulsion Em-2	0.7
Sensitizing dye III-40	1.3×10^{-5}
Sensitizing dye III-6	1.0×10^{-4}
Sensitizing dye II-40	1.0×10^{-4}
Cyan coupler C-1	0.28
Colored cyan coupler CC-1	0.05
DIR compound D-1	0.02
High boiling solvent Oil-1	0.28
Gelatin	0.6

Layer 5: High speed red-sensitive emulsion layer RH

Silver iodobromide emulsion Em-3	0.9
Sensitizing dye III-40	0.8×10^{-5}
Sensitizing dye III-6	0.6×10^{-4}

Magenta coupler M-2	0.04
Colored magenta coupler CM-1	0.04
DIR compound D-2	0.018
High boiling solvent Oil-2	0.20
Gelatin	0.8

Layer 9: High speed green-sensitive emulsion layer GH

Silver iodobromide emulsion Em-3	0.9
Sensitizing dye IV-14	2.2×10^{-4}
Sensitizing dye I-5	2.4×10^{-5}
Magenta coupler M-2	0.04
Magenta coupler M-3	0.04
Colored magenta coupler CM-2	0.04
DIR compound D-2	0.008
High boiling solvent Oil-2	0.15
Gelatin	0.9

Layer 10: Yellow filter layer YC

Yellow colloidal silver	0.12
Anti-color staining agent SC-1	0.1
High boiling solvent Oil-2	0.13
Gelatin	0.8
Formalin scavenger HS-1	0.09
Formalin scavenger HS-2	0.07

Layer 11: Low speed blue-sensitive emulsion layer BL

Silver iodobromide emulsion Em-1	0.35
Silver iodobromide emulsion Em-2	0.15

Layer 14: Second protective layer Pro-2

Alkali-soluble matting agent (average grain size 2 μm)	0.07
Polymethyl methacrylate (average grain size 3 μm)	0.03
Lubricant WAX-1	0.04
Gelatin	0.6

The emulsions used to prepare the sample described above are as follows:

Em-1

Emulsion containing monodispersed (individual grain silver iodide content relative standard deviation 18%) silver iodobromide grains having an average grain size of 0.35 μm, an average silver iodide content of 6.0 mol% and a core of 35 mol% AgI.

Em-2

Emulsion containing monodispersed (individual grain silver iodide content relative standard deviation 19%) silver iodobromide grains having an average grain size of 0.5 μm, an average silver iodide content of 6.8 mol% and a core of 35 mol% AgI.

Em-3

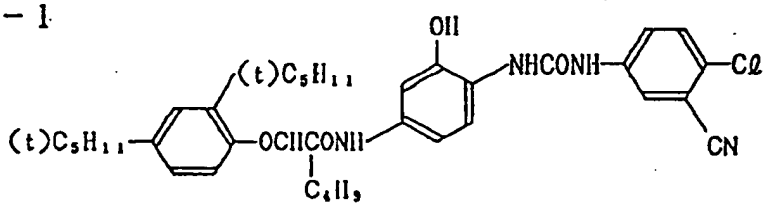
Emulsion containing monodispersed (individual grain silver iodide content relative standard deviation 18%) silver iodobromide grains having an average grain size of 0.65 μm, an average silver iodide content of 8.0 mol% and a core of 35 mol% AgI.

Em-4

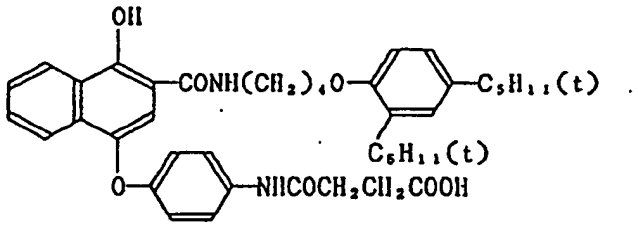
Emulsion containing monodispersed silver iodobromide grains having an average grain size of 0.8 μm, an average silver iodide content of 8.0 mol% and a twin plane of an aspect ratio of 3.5.

The compounds used to prepare the sample described above are as follows:

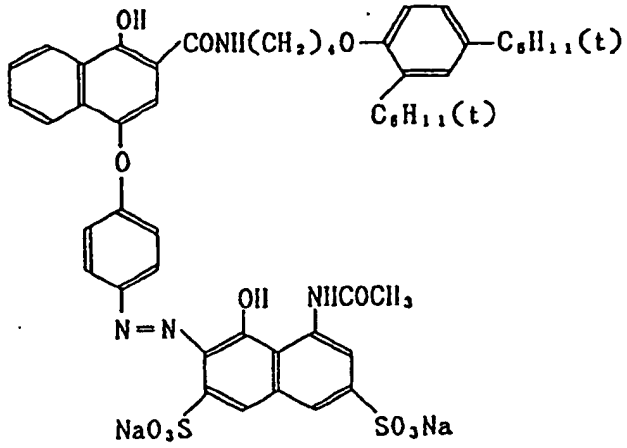
C – 1



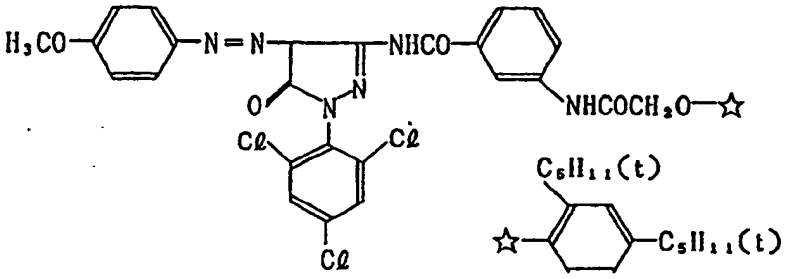
C – 2



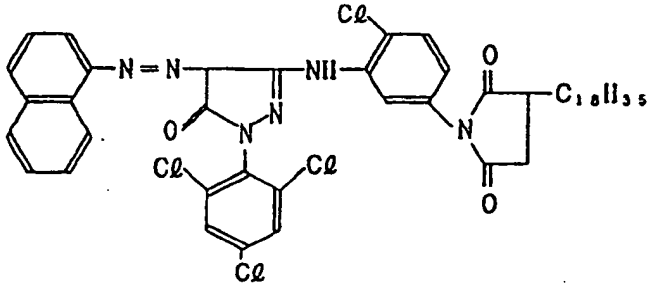
CC－1



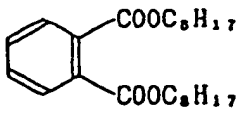
CM－1



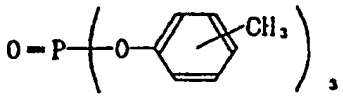
CM－2



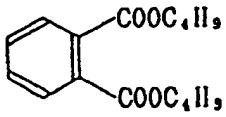
Oil-1



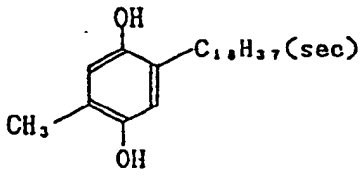
Oil-2



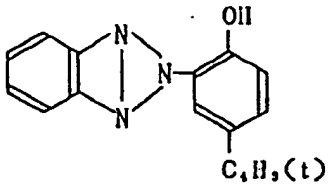
Oil-3



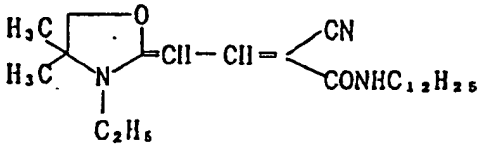
SC-1



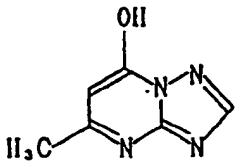
UV-1



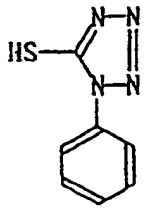
UV-2



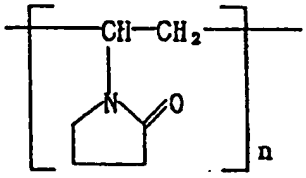
S T − 1



A F − 1



A F − 2



n: Degree of polymerization

In addition to these compositions, a coating aid Su-1, a dispersing agent Su-2, a viscosity regulator, hardeners H-1 and H-2, a stabilizer ST-1, an antifogging agent AF-1 and two kinds of AF-2 having an average molecular weight of 10,000 or 1,100,000, respectively, were added.

The average grain size of silver halide in the emulsions used for the sample described above is expressed as a cube diameter.

Each emulsion was optimally sensitized with gold and sulfur.

Next, sample Nos. 102 through 106 were prepared in exactly the same manner as in sample No. 101 except that the sensitizing dyes for Layers 3, 4, 5, 8 and 9 were altered to those listed in Table 1. The total addition amount of sensitizing dyes listed in Table 1 in each layer is the same in sample Nos. 101 through 106.

Thus, the total amount differences among samples are based on combinations of sensitizing dyes and molar ratios thereof.

Each emulsion contained in sample Nos. 101 through 106 was optimally chemically sensitized with a gold and sulfur sensitizer by an ordinary method.

To determine the spectral sensitivity distribution, color development was conducted by the process described below, followed by spectral exposure, and each parameter of spectral sensitivity distribution was measured at a density of D_{min} + 0.3.

The results are given in Table 1.

In the process, running was carried out until th replenisher was fed in an amount 3 times th capacity of the stabilization tank.

Potassium carbonate	40 g
Sodium hydrogen carbonate	3 g
Potassium sulfite	7 g
Sodium bromide	0.5 g
Hydroxylamine sulfate	3.2 g
4-amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline sulfate	6.0 g
Diethylenetriamine pentaacetate	3.0 g
Potassium hydroxide	2 g

Water was added to make a total quantity of 1ℓ, and potassium hydroxide or 20% sulfuric acid was used to obtain a pH of 10.12.

The composition of the bleacher used is as follows:

Disodium ethylenediaminetetraacetate	2 g
Ammonium bromide	150 g
Glacial acetic acid	40 mℓ
Ammonium nitrate	40 g

Water was added to make a total quantity of 1ℓ, and aqueous ammonia or glacial acetic acid was used to obtain a pH of 4.5.

The composition of the bleacher replenisher used is as follows:

Ferric ammonium 1,3-diaminopropanetetraacetate	0.40 mol
Disodium ethylenediaminetetraacetate	2 g
Ammonium bromide	170 g
Ammonium nitrate	50 g
Glacial acetic acid	61 mℓ

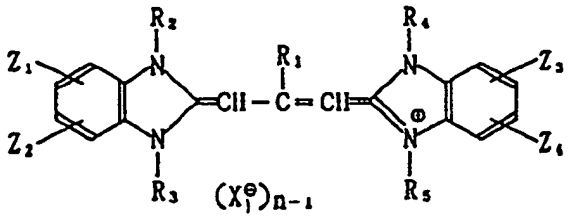
Water was added to make a total quantity of 1ℓ, and aqueous ammonia or glacial acetic acid was used to obtain a pH of 3.5, with proper adjustment made to maintain a given pH level of the bleacher tank solution.

The composition of the fixer and fixer replenisher used is as follows:

Table 1

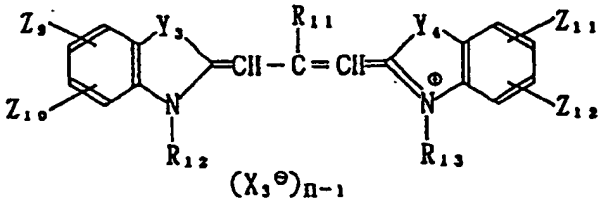
Sample No.	Sensitizing dyes for layers 3, 4 and 5 (dye addition amount, mol%)	Sensitizing dyes forlayers 8 and 9 (dye addition amount, mol%)	λ_{Rmax} (nm)	S_{R610}/S_{Rmax} (%)	λ_{Gmax} (nm)	S_{G545}/S_{Gmax} (%)	Grey balance under fluorescent lamp lighting[1]		Print color features[2]	Remark
							$\Delta\Delta S_R$	$\Delta\Delta S_G$		
101	III-40 6 III-6 47 II-40 47	IV-14 90 I-5 10	633	75	553	87	-0.20	+0.12	Skin color with marked bluish green.	Comparative
102	III-6 60 I-5 40	IV-14 90 I-5 10	628	82	553	87	-0.12	+0.12	Skin color with bluish green, lacking liveliness.	Comparative
103	III-6 30 I-5 70	IV-14 90 I-5 10	615	97	553	87	-0.02	+0.12	Skin color with green, lacking liveliness.	Comparative
104	III-6 30 I-5 70	IV-14 80 I-5 20	615	97	556	76	-0.02	+0.05	Naturalistic skin color with no significant difference from strobe light print.	Inventive
105	III-6 30 I-5 70	IV-14 70 I-5 30	615	97	563	65	-0.02	+0.01	Naturalistic skin color. Skin color with slight yellow in strobe light print.	Inventive
106	III-6 60 I-5 40	IV-14 80 I-5 20	628	82	556	76	-0.12	+0.05	Skin color with blue, lacking liveliness.	Comparative

formula I



wherein R_1 represents a hydrogen atom, an alkyl group or an aryl group; R_2, R_3, R_4 and R_5 independently represent an alkyl group or an aryl group; Z_1, Z_2, Z_3, and Z_4 independently represent a hydrogen atom, a halogen atom, a hydroxyl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an acyloxy group, an aryloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkoxycarbonylamino group, a carbamoyl group, an aryl group, an alkyl group, a cyano group or a sulfonyl group; Z_1 and Z_2 and / or Z_3 and Z_4 may link together to form a ring; X_1 represents an anion; n represents an integer 1 or 2, provided that, when the sensitizing dye forms an intramolecular salt, n represents 1.

formula III



wherein R_{11} represents a hydrogen atom, an alkyl group or an aryl group; R_{12} and R_{13} independently represent an alkyl group or an aryl group; Y_3 and Y_4 independently represent a sulfur atom or a selenium atom; Z_9, Z_{10}, Z_{11}, and Z_{12} independently represent a hydrogen atom, a halogen atom, a hydroxyl group, an alkoxy group, an amino group, an acyl group, an acylamino group, an acyloxy group, an aryloxy group, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkoxycarbonylamino group, a carbamoyl group, an aryl group, an alkyl group, a cyano group or a sulfonyl group; Z_9 and Z_{10} and / or Z_{11} and Z_{12} may link together to form a ring; X_3 represents an anion; n represents an integer 1 or 2, provided that, when the sensitizing dye forms an intramolecular salt, n represents 1.

5. The material of claim 4, wherein the red-sensitive emulsion layer contains the sensitizing dye represented by formula I in an amount of 10 to 90 mol% based on the total amount of a sensitizing dye in the red-sensitive emulsion layer.

6. The material of claim 4, wherein the red-sensitive emulsion layer contains the sensitizing dye represented by formula I in an amount of 60 to 90 mol%, based on the total amount of a sensitizing dye in the red-sensitive emulsion layer.

7. The material of claim 4, wherein the green-sensitive emulsion layer contains said oxacabocyanine, oxabenzimidazolecyanine, thia-4' -cyanine or thia-2' -cyanine dyes in an amount of 50 to 85 mol% based on the total amount of a sensitizing dye in the green-sensitive emulsion layer.

8. The material of claim 4, wherein the red-sensitive emulsion layer further comprises a sensitizing dye represented by the following formula II :

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 1960

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X,Y	JP-A-621604499 (FUJI) * the whole document *	1-9	G03C7/30
Y	EP-A-0115304 (FUJI) * page 19, line 3 - page 32, line 2 *	1-9	
Y	US-A-4028115 (HINATA ET AL.) * column 2, line 24 - column 13, line 37 *	1-9	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 APRIL 1991	MAGRIZOS S.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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